Naringin Extraction from Exhausted Bergamot Peels*

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Bergamot peels contain quantities of the flavonoid naringin, which has interesting pharmacological properties. This paper describes a process using ultrafiltration and resin adsorption to purify naringin obtained by hot water extraction from bergamot peels. Utilization of bergamot wastes for production of flavonoids represents an important added value to the citrus industry.

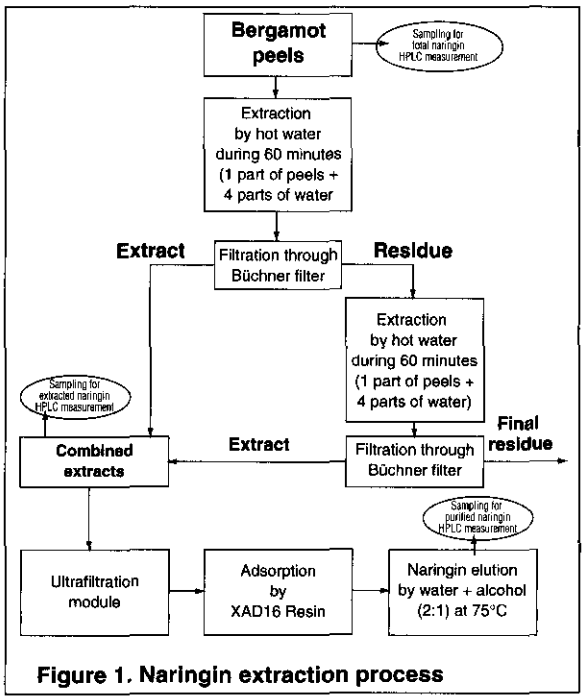

Figure 1. Naringin extraction process

Naringin in Bergamot

Bergamot (*Citrus bergamia* Risso), an extraordinary citrus that grows almost exclusively in Calabria, provides a valuable essential oil, well known and valued by perfumers around the world. Moreover, it is a rich source of important substances for the human diet. Its juice contains sugars, vitamins, free amino acids, proteins, minerals, flavonoids and carotenoids. The naringin content is responsible for the bitter taste of the juice, but it is possible to reduce the quantity of naringin by a physical process based on resin adsorption.[1]

When the bergamot fruits are processed for essential oils and juice production, about 40% of their weight remains in the form of peel, pulp, rag and seeds. This material, considered waste, is fed to cattle or dried and sent to other factories for pectin production. But these waste materials also are the interesting raw materials for the production of a large number of specialty products that are of economic value and have a potential market.

The bergamot industry is currently facing difficulties because it relies too heavily on the marketing of bergamot essential oil, which is the most profitable product of the industrial processing of bergamot fruit. To avoid dependence on this single product, the industry should develop the potential of the other bergamot by-products with high added value.

The citrus flavonoid compounds have been available commercially for a long time, but there is continuing interest in their potential for pharmaceutical use and for the manufacture of the sweet nonnutritive dihydrochalcones.

Recent research carried out by Stazione Sperimentale shows useful processes for extracting naringin from grapefruit peels and for manufacturing naringin and neohesperidin dihydrochalcones.[2-4]

Naringin content in the bergamot fruit decreases as the fruit matures, and the quantity of naringin is greater in the peel than in the endocarp.[5]

Naringin differs from hesperidin. It is more bitter than hesperidin, and, because it is more soluble than hesperidin in hot water, it can be prepared easily by extracting bergamot peel with hot water. Then the peel can be reused for pectin extraction.

Naringin Extraction

From three different trees of the same cultivar growing

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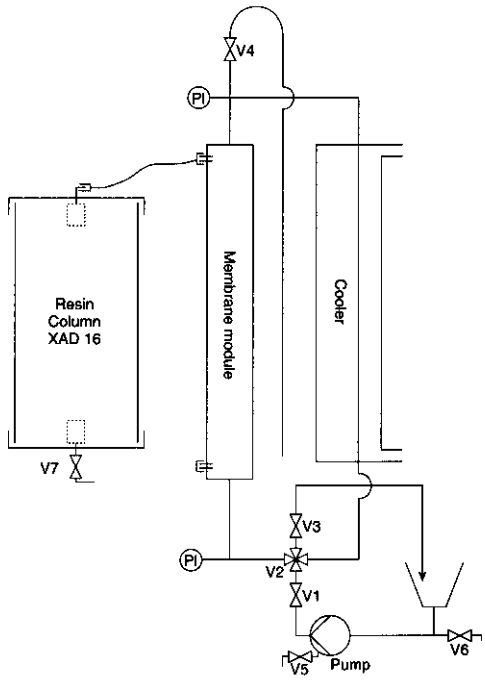

Figure 2. Verind setup for purification of naringin by adsorption on Amberlite XAD 16 resin and elution by water and alcohol

in Melito Porto Salvo (Reggio Calabria), Italy, bergamot fruits were picked between October 15 and December 18, 1995. The naringin extraction process is shown in Figure 1.

The fruits were cut in half, and a special knife was used to separate the peel from the endocarp. This process, called *ca atura*, produces 4-5 kg of peels from 20 kg of fruit. The peels were ground, combined with four times their weight of water and boiled for 60 minutes.

The peels solution was vacuum filtered, and the extract set aside. The residue was mixed with another four parts by weight of water and boiled for another 60 minutes, then vacuum filtered. The two extracts were combined and then evaporated under vacuum to reduce them to a volume consistent with the working capacity of the ultrafiltration module.

The combined and reduced extract was treated in a Verind adsorption setup (Figure 2) with Amberlite XAD 16† resin to purify the naringin. The setup included an ultrafiltration module connected to a stainless steel column that held a two-liter volume of resin. Amberlite XAD 16 resin (macroporous cross-linked polystyrene) was selected for naringin adsorption from the water fraction because its composition is consistent with FDA *CFR* 173.65 directives for separating organic substances from aqueous foods. The properties of the resin are listed in Table I.

Elution from the column was carried out with 30% ethanol, three or four times the volume of resin. Eluted solution was evaporated under vacuum and left standing until naringin crystals were no longer produced.

The spent resin was regenerated as follows: 1% solution of NaOH; hot deionized water; 1% solution of phosphoric acid; hot deionized water rinse.

†Amberlite XAD 16 is a trade name of Rohm & Haas Company

Table 1. Selected properties of Amberlite XAD 16

Physical form	**white beads**
Moisture retention	64- 60%
Bead size	0.3-1.2 mm
Specific gravity	approximately 1.02
Bulk density	710 g/l
Surface area	minimum 750 m^2/g
Pore volume	0.58-0.63 ml pore/ml of bead
pH range	0-14
Temperature limitation	180°C

Naringin Measurements

At three points in the procedure as shown in Figure 1, the naringin content was determined by HPLC using a Hewlett-Packard Model 1090 chromatograph with photodiode array detector under the following conditions:

Column	Hypersil ODS 200 mm x 4.6 mm
Sol entsystem	water:acetonitrile (75:25)
Flow rate	0.7 ml/min
Detector	287 nm
Volume	10 microliter
Internal standard	coumarin

Samples were prepared for the three measurements as follows:

- For measuring "total naringin," a solution was formed by treating 15 g of peels with 50 ml of dimethylformamide:water (1:1); 0.5 ml of this solution was used. (Solution A)
- For measuring "extract naringin," 5 ml of the solution from the combined extracts was used. (Solution B)
- For measuring "purified naringin," 5 ml of the solution eluted from the resin column was used. (Solution C)

Solution A, B or C above was placed in a 25 ml volumetric flask with 5 ml of coumarin solution (100 ppm in acetonitrile). The flask was filled to the mark with dimethylformamide:water (1:1).

Results

The naringin content in the bergamot peels varies between 2.33 and 2.94 g/kg and it decreases from October to

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Table II. Naringin extraction

Sample date (1995)	Fruits kg	Peels kg	Naringin Total g	Naringin Extracted g	Naringin Yield %
Oct 17	20.50	5.24	15.40	12.88	83.60
Oct 29	19.50	5.02	13.20	10.50	79.50
Nov 12	21.30	4.81	11.57	8.54	73.80
Dec 4	21.00	5.06	12.76	11.90	93.30
Dec 18	20.60	4.72	11.00	10.21	92.80

Table III. Naringin purification

Sample date (1995)	Naringin Processed g	Naringin Purified g	Naringin Yield %
Oct 17	12.00	11.44	95.30
Oct 29	8.40	8.00	95.20
Nov 12	7.68	7.12	92.70
Dec 4	10.86	10.20	93.90
Dec 18	9.70	8.98	92.60

December (Table II). Naringin extraction solution has high viscosity due mainly to the pectin and saccharides that interfere with the precipitation of naringin crystals. Therefore, the hot water naringin extraction process had to be supplemented by resin purification. A water-alcohol solution was used to elute naringin from the resin.

By preliminary tests, we were able to establish that the resin has a retention capacity of about 6-7 grams of naringin on a liter of resin.

In the extraction solution, the essential oil content is very low (0.01%), even if undeoiled fruits are used. With essential oils at such low levels, there is no risk of resin column damage.

As Table II shows, the efficiency of the extraction method is satisfactory. The naringin yield varies between 73.8 and 93.3%. The yield may be increased by using an alcohol-water solution in the extraction process, but then the residue cannot be used for pectin recovery.

Table III shows the results of the naringin purification. The recovery rates vary from 92.6 to 95.3%.

Summary

The method described was effective in removing the naringin from the bergamot peels and in separating it from the components of the peel that are soluble in hot water (sugars, acids, pectins, minerals). Moreover, the residue from hot water extraction can be used for pectin recovery without pretreatment.

At present, we are continuing our research by examining residues from industrial bergamot processing. These residues differ from the material used in the present work because they contain additional ingredients, such as pulp, rag, seeds and juice absorbed from the albedo.

From the results, it seems that the method described here can be useful in a reorganized bergamot industry. It must be kept in mind that the added value of wastes, especially through recovery of naringin, represents a very important aspect of the broader bergamot economy.

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